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(54) Cosmetic compositions for dyeing or for bleaching hair

(57) A cosmetic composition suitable for dyeing or bleaching hair when mixed with an oxidizing solution, comprising, in an aqueous medium:

- (a) at least one fatty acid soap,
- (b) at least one cationic or amphoteric silicone polymer,
- (c) at least one cationic surface-active agent,
- (d) at least one alkylating agent, and
- (e) at least one cationic polymer which is a quaternary polyammonium polymer, a vinyl-pyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymer (quaternized or not quaternized), a poly(methacrylamidopropyltrimethylammonium chloride), a cationic protein, a polyaminoamide, a crosslinked polyaminoamide, an alkylated polyaminoamide or a mixture thereof can be used to bleach hair or, if it additionally comprises an oxidation dye precursor and, if desired, a coupler and a reducing agent, can be used to dye hair.

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SPECIFICATION

Cosmetic compositions for dyeing or for bleaching hair

5 The present invention relates to cosmetic compositions for dyeing or for bleaching hair intended to be diluted with an oxidizing solution at the time of use, and to their application to hair.

In the technique for dyeing hair commonly called "permanent dyeing", oxidation dye precursors dissolved in a substrate with a basic pH and containing a reducing agent are used, these dye precursors being converted into dyes in the hair by condensation in the presence of an 10 oxidizing agent which is generally hydrogen peroxide, the oxidizing agent being added to the substrate just before the application to hair.

In a technique for slight bleaching or lightening of hair, an ammoniacal oxidizing composition is prepared just before use by mixing the oxidizing agent with an ammoniacal substrate is employed. If it is desired to obtain a higher degree of bleaching, a persalt, which is generally an 15 alkali metal persulphate, is added to the ammoniacal oxidizing composition just before use.

Compositions for dyeing or for bleaching hair, also called dyeing or bleaching substrates, are generally in the form of creams, shampoos or gels.

Dyeing compositions or substrates which contain at least one fatty acid, at least one particular 20 cationic polymer of the quaternary ammonium polymer type, benzyl alcohol and an alkaliifying agent have been described in French Patent No. 2,402,446. This dyeing substrate is in the form of a stiff gelled cream which adheres well to hair and makes the hair easy to disentangle and 25 pleasant to touch.

However, because of its consistency, this substrate is sometimes difficult to spread throughout the hair from the roots to the tips.

25 We have discovered a dyeing or bleaching substrate which is slightly foamy which enables the compositions to be spread very easily throughout the hair, by first restricting it to the undyed roots and then by spreading it easily up to the tips. This composition significantly improves the cosmetic properties of hair and especially the detangling of wet and dried hair, which acquires a very silky touch.

30 The present invention provides a cosmetic composition suitable for dyeing or bleaching hair which can remain stable during storage and which can be slightly foamy, intended to be diluted or mixed with an oxidizing solution at or shortly before the time of use, comprising, in an aqueous medium:

- 35 a) at least one fatty acid soap,
- b) at least one cationic or amphoteric silicone polymer,
- c) at least one cationic surface-active agent,
- d) at least one alkaliifying agent, and
- e) at least one cationic polymer which is a quaternary polyammonium polymer or "ionene", a vinylpyrrolidone dialkylaminoalkyl acrylate or methacrylate copolymer (quaternized or otherwise), a 40 poly(methacryl-amido propyltrimethylammonium chloride), a cationic protein or a polyaminoamide which may be crosslinked or alkylated,

45 or a mixture thereof.

When the composition or substrate is used in a dyeing composition, at least one oxidation dye precursor and at least one reducing agent are added. In this case a cationic polymer which is a cationic cyclopolymer may also be used.

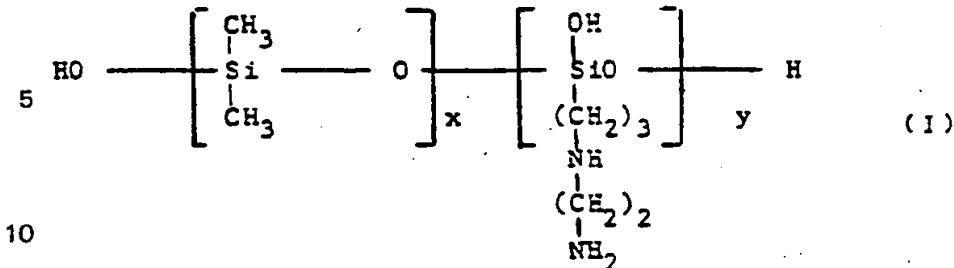
The fatty acid soaps used according to the invention are preferably alkali metal salts or alkanolamine salts (such as monoethanolamine, diethanolamine, triethanolamine, 2-amino-2-methyl-1-propanol, 2-amino-2-methyl-1,3-propanediol or triisopropanolamine) of C₁₂-C₁₈ fatty acids, the fatty chain of which can be saturated or unsaturated. Examples of fatty acids are lauric, 50 palmitic, oleic and myristic acids.

55 Triethanolamine, monoethanolamine and 2-amino-2-methyl-1-propanol salts of lauric, palmitic and oleic acids are the particularly preferred soaps.

The cationic or amphoteric silicone polymers used according to the invention are preferably polysiloxanes in which one or more of the silicon atoms on the chain carries an aliphatic amino 55 group whose amine group is primary, secondary, tertiary, quaternary or is betainized. The term "aliphatic amino" covers aminoalkyl and aminohydroxyalkyl groups, the alkyl chain of which may optionally be interrupted by one or more nitrogen or oxygen atoms.

Cationic silicone polymers are described especially in the CTFA dictionary (3rd edition, 1982, published by The Cosmetic, Toiletry and Fragrance Association, Inc.).

60 The more preferred cationic silicone polymers are those of formula:



15 in which x and y, which may be identical or different, are integers such that the average molecular weight of the polymer is from 5,000 to 10,000. This polymer is also called "amodimethicone".

Other cationic silicone polymers which can be used according to the invention are those of formula:

$$20 \quad (R_1)_a G_{3-a} - Si(-OSiG_2)_n - [OSiG_b(R_1)_{2-b}]_m - O - SiG_{3-a}(R_1)_a$$

in which
G is hydrogen or a phenyl, OH, or C₁–C₈ alkyl group, preferably a methyl group;

25. a is an integer from 0 to

b is 0 or 1, preferably 1;
n is a number from 0 to 1,999, preferably from 49 to 149 and m is a number from 1 to 2,000, preferably from 1 to 10, such that the sum n+m is a number from 1 to 2,000, preferably from 50 to 150;

R₁ is a monovalent group of formula C_qH_{2q}L in which q is an integer from 2 to 8 and L is a group of formula:

$$-\text{N}(\text{R}_2)\text{CH}_2-\text{CH}_2-\text{N}(\text{R}_2)_2,$$

$$-N(R_2)_2.$$

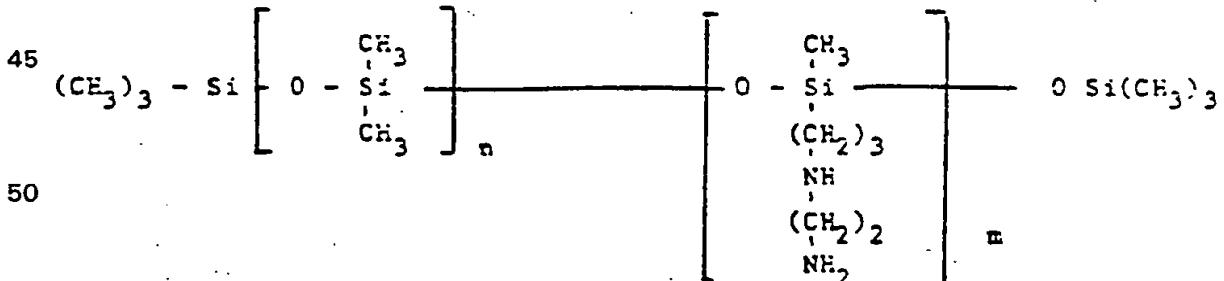
$$-\bullet N(R_2)_3 A^\bullet,$$

35 $-\ddot{\sigma}N(R_2)H_2A^\ddot{\sigma}$, or

$$-\text{N}(\text{R}_2)\text{CH}_2-\text{CH}_2-\text{NR}_2\text{H}_2\text{A}^+$$

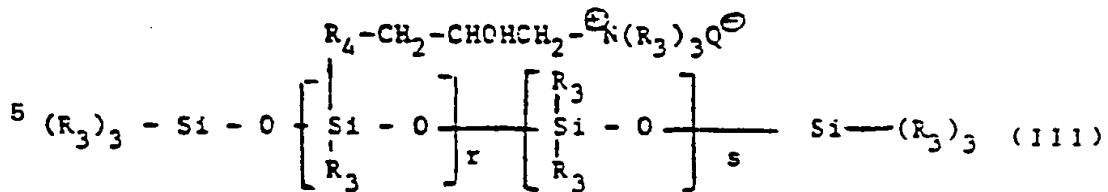
in which R_2 is hydrogen or a phenyl, benzyl or saturated hydrocarbon group, preferably an alkyl group containing from 1 to 20 carbon atoms, and A^\ominus is a halide ion.

40 These compounds are described in greater detail in European Patent Application No. 95,238. A particularly preferred polymer of this formula "trimethylsilylamodimethicone" is of formula:



55 wherein n has a value of from 0 to 1,999, preferably from 49 to 149, and m has a value of from 1 to 2,000, preferably from 1 to 10, such that $m+n$ has a value of from 1 to 2,000, preferably from 50 to 150.

Other cationic silicone polymers which may be used according to the invention are of formula:



10 in which:

R₃ is a monovalent hydrocarbon group containing from 1 to 18 carbon atoms, preferably an alkyl or alkenyl group such as a methyl group;

R₄ is a hydrocarbon group optionally containing a chain oxygen atom, preferably a C₁-C₁₈ alkylene group or a C₁-C₁₈, more preferably C₁-C₈, alkyleneoxy group;

15 Q⁰ is a halide ion, preferably chloride;

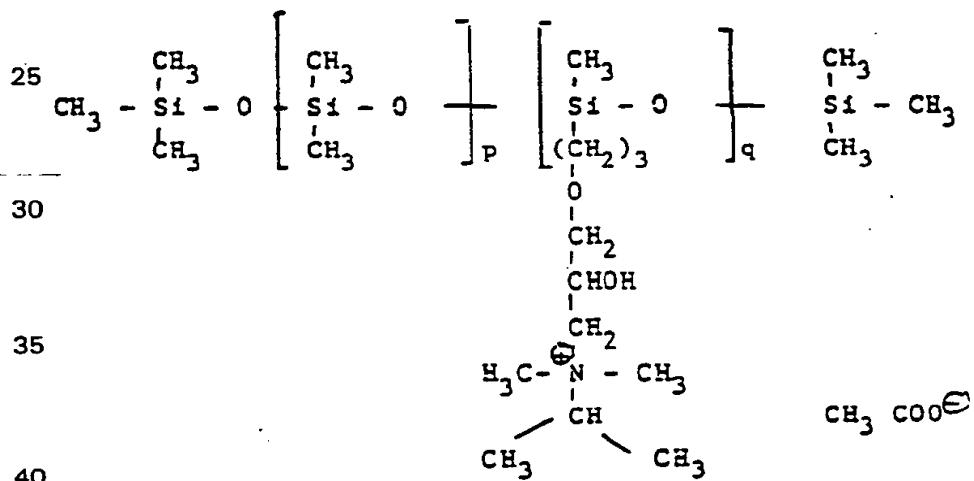
r has a statistical mean value of from 2 to 20, preferably of from 2 to 8; and

s has a statistical mean value of from 20 to 200, preferably of from 20 to 50.

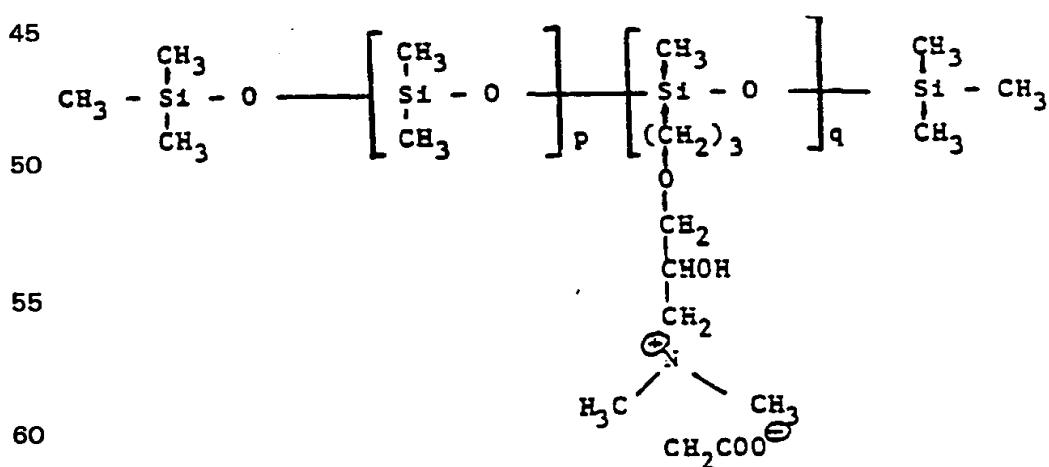
These compounds are described in greater detail in US Patent 4,185,087.

15 A particularly preferred polymer of this class is that sold by Union Carbide under the name 20 "Ucar Silicone ALE 56".

It is also possible to use a cationic silicone polymer of formula:



sold under the trade name Abil 9905 by Goldschmidt or an amphoteric silicone polymer of formula:



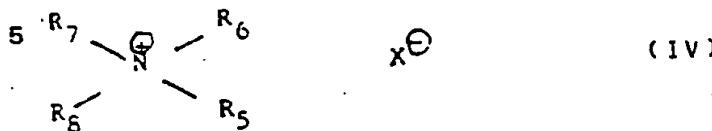
65 sold under the trade name Abil 9950 by Goldschmidt;

65 wherein, in each case, p and q are such that the average molecular weight of each product is

65

from 1,000 to 8,000.

The cationic surfactants used according to the invention preferably have the formula (IV):



10 in which:

(1) R_5 and R_6 are both methyl groups,

i) R_7 and R_8 , which may be identical or different, are each a linear aliphatic group, preferably an alkyl group containing from 12 to 22 carbon atoms or an aliphatic group derived from a tallow fatty acid containing from 14 to 22 carbon atoms,

15 ii) R_7 is a straight-chain aliphatic group, preferably an alkyl group containing from 14 to 22 carbon atoms, and R_8 is a methyl or benzyl group,

iii) R_7 is an alkylamidopropyl (C_{14} – C_{22} alkyl) group and R_8 is an alkylacetate (C_{12} – C_{16} alkyl) group,

iv) R_7 is a γ -gluconamidopropyl group, an aliphatic group derived from a tallow fatty acid or a

20 C_{16} – C_{18} alkyl group and R_8 is a hydroxyethyl group, and X^- is an anion such as a halide or methosulphate ion;

(2) R_5 is an alkylamidoethyl or alkenylamidoethyl group, wherein the alkyl or alkenyl moiety contains from 14 to 22 carbon atoms and originates from a tallow fatty acid,

R_6 and R_7 form, together with the nitrogen to which they are attached, a 2-alkyl-4,5-dihydroimidazole heterocyclic ring wherein the alkyl moiety is derived from a tallow fatty acid,

R_8 is a methyl group, and

X^- is a methosulphate ion; or

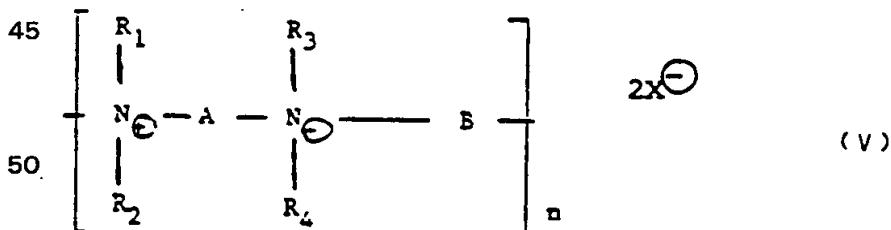
(3) R_5 , R_6 and R_7 form, together with the nitrogen to which they are attached, a six membered aromatic heterocyclic ring, R_8 is a C_{14} – C_{18} alkyl group and X^- is a halide anion.

30 Preferred cationic surface-active agents are: dimethylalkyl- (C_{18}) ammonium chloride sold under the name "Genamine DSAC" by Hoechst, trimethylalkyl- $(C_{20}$ – $C_{22})$ ammonium chloride sold under the trade name "Genamine KDM-F" by Hoechst, cetylpyridinium chloride, dimethyldialkyl(C_{12} – C_{14}) ammonium chloride, dimethyl- γ -gluconamidopropylhydroxyethylammonium chloride sold under the name "Ceraphyl 60" by Van Dyk, dimethyldicetylammonium chloride sold under the trade name

35 "Norarium M2 SH", dimethyl dialkyl ammonium chloride sold under the trade name "Norarium M2 CD", dimethylhydroxyethylalkyl(tallow)ammonium chloride, dimethyl dialkyl (hydrogenated tallow)ammonium chloride sold under the trade name ARQUAT 2H 75, dimethylhydroxyethylcetylammonium chloride and dimethylstearylbenzylammonium chloride sold under the trade names "Ammonyx 4002" by Onyx or "Catigene CS 40" by Stepan. The cationic polymers used

40 according to the invention are preferably:

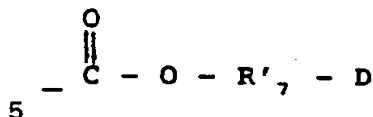
1) quaternary ammonium polymers consisting of recurring repeat units, which may be identical or different, of formula (V):



wherein:

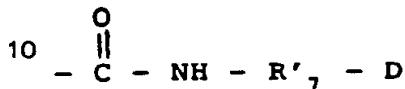
55 R_1 , R_2 , R_3 and R_4 , which may be identical or different, are each an aliphatic, alicyclic or arylaliphatic group containing from 1 to 20 carbon atoms or a C_1 – C_6 , preferably C_1 – C_4 , hydroxyaliphatic group, or at least one of a pair of R_1 and R_2 and/or R_3 and R_4 form, together with the nitrogen to which they are attached, a heterocyclic ring optionally containing a second heteroatom other than nitrogen, or

60 R_1 , R_2 , R_3 and R_4 , which may be identical or different, are each a linear or branched C_2 – C_6 alkyl group substituted by a nitrile, ester, acyl or amide group or by a group of formula:



5

or



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wherein:

R' is an alkylene group, and

15 D is a quaternary ammonium group;

15

A and B, which may be identical or different, are each an aliphatic hydrocarbon group containing from 2 to 20 carbon atoms, which is linear or branched, saturated or unsaturated and which optionally contains, inserted into the main chain, one or more aromatic rings or one or more oxygen or sulphur atoms or one or more sulfoxide, sulphone, disulphide, amine, alkylamine, quaternary ammonium, hydroxyl, ureido, amide or ester groups; or

20

20 A, R₁ and R₃, together with the two nitrogen atoms to which they are attached, form a piperazine ring;

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each X^o, which may be identical or different, is an anion derived from an inorganic or organic acid; and

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25 n is such that the molecular mass of the polymer is from 1,000 to 100,000.

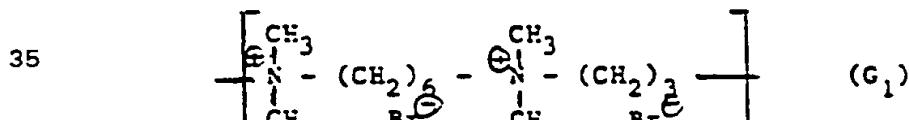
Polymers of this type are described, in particular, in French Patents 2,320,330, 2,270,846 and 2,316,271 and in US Patents 2,273,780, 2,375,853, 2,388,614, 2,454,547, 3,206,462, 2,261,002 and 2,271,378.

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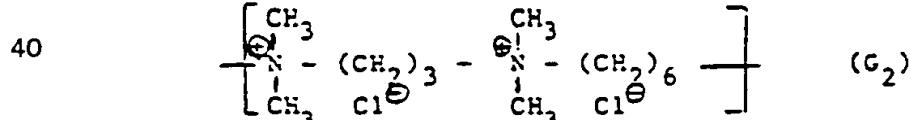
Other polymers of this type are described in US Patents 3,874,870, 4,001,432, 3,929,990, 30 3,966,904 and 4,005,193.

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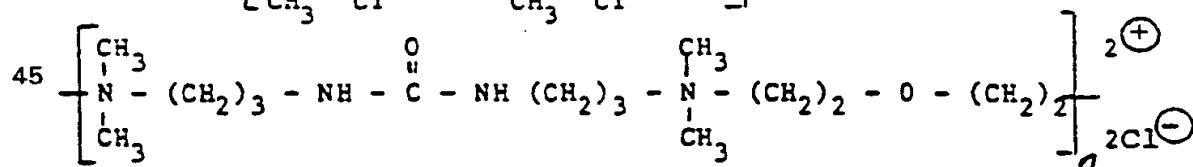
Other preferred polymers are those which contain one of the following repeat units:



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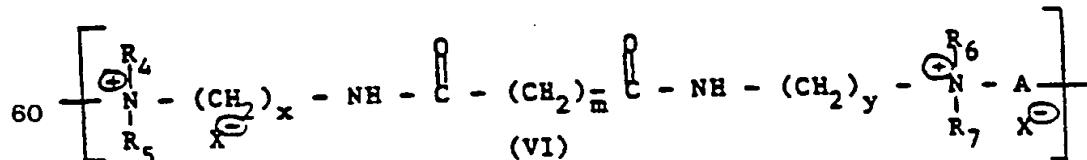
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50 in which n is approximately 6 and which is sold under the name "Mirapol A 15" by Miranol; and poly(dimethylbutenylammonium chloride)- α,ω -bis-(triethanolammonium chloride) sold under the trade name "Onamer M" by Onyx Chemical.

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55 2) Quaternary ammonium polymers consisting of repeat units, which may be identical or different, of formula (VI):

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wherein:

65 R₄, R₅, R₆ and R₇, which may be identical or different, are each hydrogen, a methyl, ethyl,

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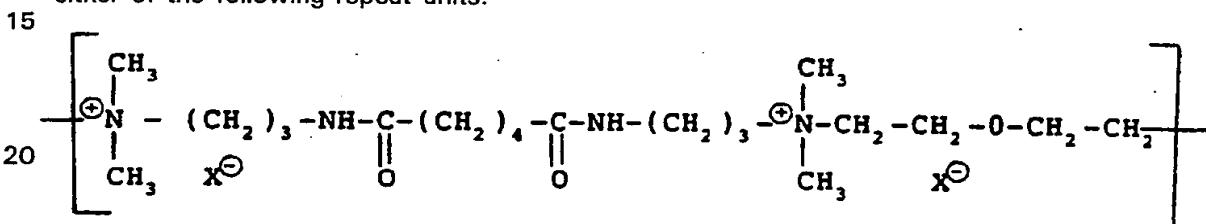
propyl, 2-hydroxyethyl or 2-hydroxypropyl group or a group of formula $-\text{CH}_2-\text{CH}_2-(\text{O}-\text{CH}_2-\text{CH}_2)_p-\text{OH}$ in which p is an integer from 0 to 6;
 with the proviso that R_4 , R_5 , R_6 and R_7 are not all simultaneously hydrogen;
 x and y , which may be identical or different, are each integers from 1 to 6;
 5 m is an integer from 0 to 34;
 each X^\ominus , which may be identical or different, is a halogen anion; and
 A is a divalent hydrocarbon group optionally containing a chain oxygen atom, preferably a group of formula:

10 $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$

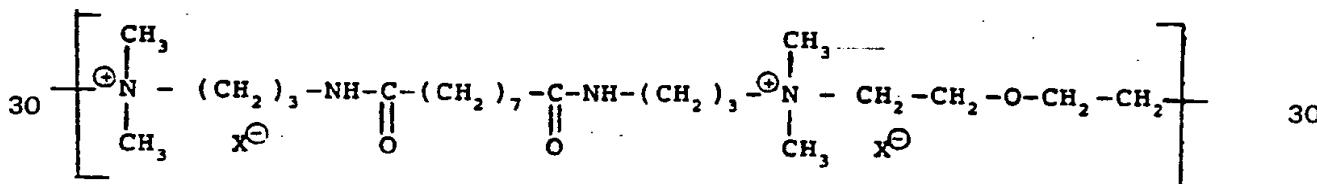
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These compounds are described in European Patent 122,324.

The quaternary ammonium polymers which are particularly preferred are those which contain either of the following repeat units:



wherein each X , which may be identical or different, is a halogen, sold under the trade name
 25 "Mirapol AD1" by Miranol, or:



35 wherein each X , which may be identical or different, is a halogen, sold under the trade name
 "Mirapol AZ1" by Miranol.

3) Poly(methacrylamidopropyltrimethylammonium chloride) sold under the trade name "Poly-maptac" by Texaco Chemicals.

4) Vinylpyrrolidinedialkylaminoalkyl acrylate or methacrylate copolymers (quaternized or otherwise), such as those sold under the trade names "Gafquat" by GAF Corporation, such as, for example, "copolymer 845" and "Gafquat 734 or 755" which are described in French Patents 2,077,143 and 2,393,573.

5) Cationic proteins which are chemically modified polypeptides which contain, either at the end of the chain or grafted onto the chain, at least one amine or quaternary ammonium group.

45 Preferred proteins are:

collagen hydrolysates containing triethylammonium groups, such as the products sold under the trade name "Quat-Pro E" by Maybrook and called "Triethonium Hydrolyzed Collagen Ethosulphate" in the CTFA dictionary (CTFA is the abbreviation for The Cosmetic, Toiletry and Fragrance Association Inc., 1110 Vermont Avenue N.W. Washington DC 20005 U.S.A., who

50 publish the "Cosmetic Ingredient Dictionary" 3rd edition);

collagen hydrolysates containing trimethylammonium or trimethylstearylammmonium chloride groups sold under the trade name "Quat-Pro S" by Maybrook and called "Steartrimonium Hydrolyzed Collagen" in the CTFA dictionary;

animal protein hydrolysates containing trimethylbenzylammonium groups, such as the products sold under the trade name "Crotein BTA" by Croda and called "Benzyltrimonium hydrolyzed animal protein" in the CTFA dictionary;

protein hydrolysates containing, on the polypeptide chain, quaternary ammonium groups containing at least one alkyl group containing from 1 to 18 carbon atoms, such as:

Croquat L, the polypeptide chain of which has an average molecular weight of approximately

60 2,500 and the quaternary ammonium group of which contains a C_{12} alkyl group;

Croquat M, the polypeptide chain of which has an average molecular weight of approximately

2,500 and the quaternary ammonium group of which contains a $\text{C}_{10}-\text{C}_{18}$ alkyl group;

Croquat S, the polypeptide chain of which has an average molecular weight of approximately

2,700 and the quaternary ammonium group of which contains a C_{18} alkyl group;

65 Crotein Q, the polypeptide chain of which has an average molecular weight of the order of

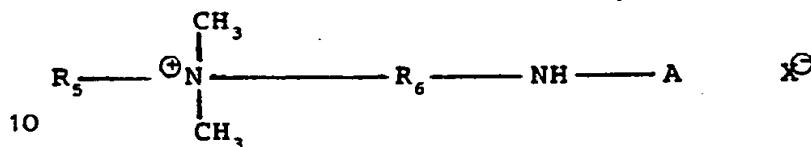
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12,000 and the quaternary ammonium group of which contains at least one alkyl group containing from 1 to 18 carbon atoms.

These different products are sold by Croda.

Other preferred quaternized proteins are those of formula:

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in which

A is a protein residue derived from a collagen protein hydrolysate,

15 R5 is a lipophilic group containing up to 30 carbon atoms,

R6 is an alkylene group containing from 1 to 6 carbon atoms, and

X[⊖] is an anion;

the protein having a molecular weight of from 1,500 to 10,000, preferably from 2,000 to 5,000. The preferred product is that sold under the trade name "Lexein QX 3000" by Inolex

20 and is called "Cocotrimonium Collagen Hydrolysate" in the CTFA dictionary.

Other preferred proteins are hydrolysates of animal proteins, which contain dimethylamine groups, which are sold under the trade name "Lexein CP 125" by Inolex and referred to under the name "Oleamidopropyl dimethylamine hydrolyzed animal protein" in the CTFA dictionary.

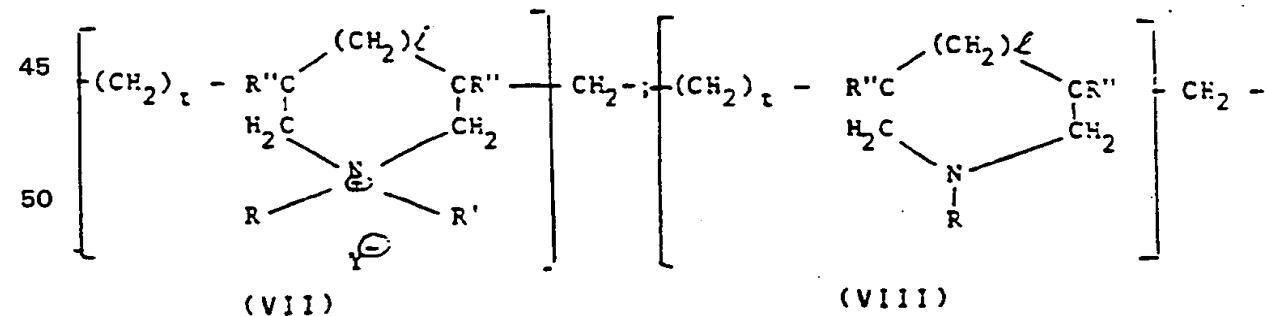
25 6) Water soluble polyaminoamides, prepared by the polycondensation of an acid compound with a polyamine. These polyaminoamides may be crosslinked and alkylated. Such polymers are described in French Patents 2,252,840 and 2,368,508.

30 Other polyaminoamides resulting from the condensation of polyalkylenepolyamines with polycarboxylic acids and which are alkylated with difunctional agents may be used, for example, adipic acid/dialkylaminohydroxyalkyl/dialkylenetriamine polymers in which the alkyl moiety contains from 1 to 4 carbon atoms. Such polymers are described in French Patent 1,583,363.

35 Examples of such derivatives are adipic acid/dimethylaminohydroxypropyl/diethylenetriamine polymers, sold under the trade names "Cartaretine F, F4 or F8" by Sandoz.

40 Further examples of polyaminoamides are those obtained by the reaction of a polyalkylenepolyamine comprising two primary amine groups and at least one secondary amine group with a dicarboxylic acid, the molar ratio between the polyalkylenepolyamine and the dicarboxylic acid being from 0.8:1 to 1.4:1, the resulting polyaminoamide subsequently being reacted with epichlorohydrin, the molar ratio of epichlorohydrin to the secondary amine groups of the polyamide being from 0.5:1 to 1.8:1. Such polymers are described in US Patents 3,227,615 and 2,961,347.

45 A group of polymers which may be used advantageously in the dye compositions comprising oxidation dye precursors and a reducing agent are cyclopolymer units of formula (VII) or (VIII):



50 55 in which:

1 and t are each 0 or 1 and the sum 1+t is 1;

each R'', which may be identical or different, is hydrogen or a methyl group;

55 R and R', which may be identical or different, are each an alkyl group containing from 1 to 22 carbon atoms, a hydroxyalkyl group in which the alkyl group preferably contains from 1 to 5 carbon atoms, or a lower amidoalkyl group, or R and R' may form, together with the nitrogen to which they are attached, a heterocyclic group such as piperidyl or morpholinyl;

60 or copolymers comprising units of formula (VII) or (VIII) and units derived from acrylamide or diacetoneacrylamide,

65 and Y[⊖] is an anion, such as bromide, chloride, acetate, borate, citrate, tartrate, bisulphate, bisulphite, sulphate or phosphate.

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Preferred cyclopolymers are a homopolymer of dimethyldiallylammonium chloride sold by Merck under the trade name "Merquat 100", which has a molecular weight of less than 100,000, and a copolymer of dimethyldiallylammonium chloride with acrylamide which has a molecular weight of more than 500,000 and which is sold under the trade name "Merquat 550" by Merck.

5 The alkaliifying agents used in accordance with the invention may, for example, be sodium or potassium hydroxide, aqueous ammonia, or alkanolamines such as those used to form the soap. These alkaliifying agents are generally used in a sufficient quantity for the pH of the substrate to be higher than 7, preferably higher than 8. Aqueous ammonia is preferred.

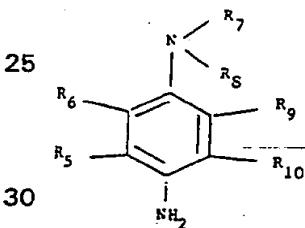
When the substrate is employed in a dye composition, it additionally contains at least one

10 oxidation dye precursor and at least one reducing agent. The reducing agent is preferably thioglycolic acid, thiolactic acid, ammonium thiolactate or sodium metabisulphite. It is preferably used in an amount of from 0.5 to 2% by weight relative to the total weight of the composition.

The oxidation dye precursors are preferably aromatic compounds of the diamine, aminophenol or phenol type.

15 Among these oxidation dyes there may be distinguished bases which are para or ortho derivatives such as diamines and mono- or diamino- phenols and compounds R5 which are known as modifiers or couplers which are meta derivatives chosen from meta-diamines, meta-aminophenols, phenols and polyphenols.

20 Examples of para-phenylenediamines which can be used in the compositions according to the invention, are primary, secondary and tertiary para-phenylenediamines, optionally substituted on the benzene ring, preferably those of formula:



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in which:

35 R₇ and R₈, which may be identical or different, are each hydrogen or a straight or branched chain lower alkyl group, mono- or polyhydroxylated alkyl, piperidinoalkyl, carbamylalkyl, dialkylcarbamylalkyl, aminoalkyl, monoalkylaminoalkyl, dialkylaminoalkyl, omega-aminosulphonylalkyl, carboxyalkyl, alkylsulphonamidoalkyl, arylsulphonamidoalkyl, morpholinoalkyl, acylaminoalkyl, sulphoalkyl or alkoxyalkyl group, in which groups the alkyl moiety preferably contains from 1 to 4 carbon atoms;

40 or R₇ and R₈ form, together with the nitrogen to which they are attached, a heterocyclic group, preferably containing 5 or 6 ring members, such as morpholine or piperidine; and

R₅, R₆, R₉ and R₁₀, which may be identical or different, are each hydrogen, a halogen or a lower alkyl group, preferably containing 1 to 4 carbon atoms, or a group of formula -OZ wherein Z is a hydroxyalkyl, alkoxyalkyl, acylaminoalkyl, carbalkoxyaminoalkyl, mesylaminoalkyl, ureidoalkyl, aminoalkyl or mono- or dialkylaminoalkyl group.

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In the above definition, halogen may mean fluorine, bromine or, preferably, chlorine.

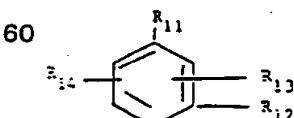
These p-phenylenediamines may be introduced into the dye composition in the form of free base or in salt form, for example in the form of their hydrochloride, hydrobromide, sulphate or tartrate salts.

50 Other oxidation bases are p-aminophenol or a homologue thereof whose aromatic nucleus is substituted by at least one methyl group or by chlorine; N-methyl-p-aminophenol, a heterocyclic derivative of piperidine or of benzomorpholine, 5-amino-indole, ortho-aminophenol, p-aminodiphenylamine or an ortho-phenylenediamine or a substituted derivative thereof. The oxidation bases are generally used in an amount of from 0.01 to 5% by weight relative to the total weight of the composition.

50

55 The dyeing compositions may contain at least one coupler, in addition to one or more oxidation bases. A preferred coupler has the formula:

55



60

65 wherein:

65

R_{11} and R_{12} , which may be identical or different, are each a hydroxyl group or a group of formula $-NHR$, wherein R is hydrogen or an acyl, ureido, carbalkoxy, carbamylalkyl, alkyl, dialkylcarbamylalkyl, hydroxyalkyl or mesylaminoalkyl group; one of R_{11} and R_{12} also being able to be hydrogen or an alkoxy or alkyl group, provided that the other is a hydroxyl group;

5 5 R_{13} and R_{14} , which may be identical or different, are each hydrogen or a halogen, an amino, alkylamino, acylamino, ureido, a branched or linear alkyl group or a group of formula OZ Wherein Z is a hydroxyalkyl, polyhydroxyalkyl, alkoxyalkyl, mesylaminoalkyl, acylaminoalkyl, ureidoalkyl or carbalkoxyalkyl group.

Other couplers which may be used in the compositions according to the invention are, for 10 example, alpha-naphthol, and heterocyclic compounds derived from benzomorpholine, pyridine, pyrazolones or diketone compounds. The couplers are generally used in an amount of from 0.001 to 5% by weight relative to the total weight of the composition. Direct dyes may be added to these oxidation dyes in order to impart highlights to the final colour.

15 The fatty acid soaps used in the compositions according to the invention are preferably present in an amount of from 1 to 25%, more preferably from 2 to 20%, by weight relative to the weight of the composition.

20 The cationic silicone polymers defined above are preferably present in an amount of from 0.05 to 5%, more preferably from 0.1 to 3%, by weight relative to the total weight of the composition.

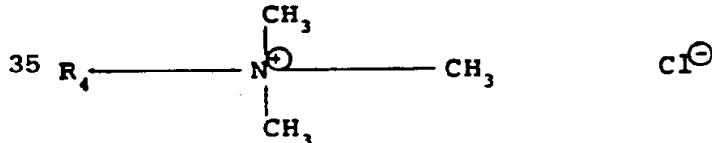
25 20 The cationic surface-active agents are preferably used in an amount of from 0.05 to 5% by weight relative to the total weight of the composition.

The cationic polymers are preferably used in an amount of from 0.05 to 5% by weight relative to the total weight of the composition.

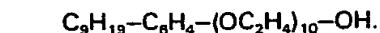
30 25 The cationic silicone polymers which are particularly preferred may be introduced into the compositions according to the invention in the form of emulsions containing the silicone polymer as well as nonionic and cationic surface-active agents.

An emulsion of this type which is particularly preferred is a composition sold under the trade name of cationic emulsion "Dow Corning 929" (DC 929) by Dow Corning and which is a combination of:

35 30 a) "amodimethicone" as hereinbefore defined;
b) trimethylalkyl(tallow)ammonium chloride of formula:

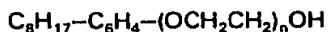


40 35 wherein R_4 is a mixture of alkenyl and/or alkyl groups containing from 14 to 22 carbon atoms, derived from a tallow fatty acid; and
c) polyoxyethylenated nonylphenol of formula:



45 45 Another emulsion based on cationic silicone polymers which can be used in the present invention is a composition sold under the trade name "Dow Corning Q2 7224" by Dow Corning and which is a combination of:

50 a) trimethylsilylamodimethicone as hereinbefore defined;
b) polyoxyethylenated octylphenol of formula:



55 55 wherein n is 40;
c) polyoxyethylenated lauryl alcohol of formula:



60 60 wherein n is 6; and
d) glycol.

The dye or bleaching agent substrates according to the invention may additionally contain various conventional adjuvants. These adjuvants may, for example, be solvents, fatty amides, natural or synthetic fatty alcohols, nonionic or amphoteric surfactants, sequestering agents, antioxidants or perfumes. The substrates or compositions according to the invention generally 65 comprise from 0 to 20% of solvents, from 0 to 15% of fatty amides, from 0 to 25% of fatty

alcohols, and from 0 to 25% of nonionic or amphoteric surfactants, relative to the total weight of the composition.

The solvents are generally lower aliphatic alcohols such as ethanol, propanol and isopropanol; glycols such as ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol and 5 hexylene glycol; glycol ethers such as methylglycol, ethylglycol, butylglycol and diethylene glycol monoethyl ether; or aromatic alcohols, especially benzyl alcohol or phenoxyethanol. 5

Examples of fatty amides are lauric, oleic or copra mono- or diethanolamides and stearic monoethanolamide.

These amides are generally used in an amount of from 0.5 to 15%, preferably from 1 to 10%, 10 by weight relative to the total weight of the composition. The natural or synthetic fatty alcohols generally contain from 10 to 18 carbon atoms and are preferably used in an amount of from 1 to 25%, more preferably from 5 to 15%, by weight relative to the total weight of the composition. 10

Examples of nonionic surfactants are C₈—C₁₈ fatty alcohols oxyethylenated with 5 to 30 moles 15 of ethylene oxide, alkylphenols oxyethylenated with 2 to 30 moles of ethylene oxide, alcohols, 1,2-alkanediols and amides polyglycerolated with 1 to 10 moles of glycerol. 15

Throughout this text, the concentrations of various constituents are relative to the composition before dilution with the oxidizing agent. By a "lower" group or moiety is meant one which generally contains from 1 to 6 or 1 to 4 carbon atoms.

20 Another subject of the invention is a hair-dyeing composition obtained by mixing the substrate specified above, containing the oxidation dye precursors and the reducing agent, with an oxidizing solution, which generally consists of hydrogen peroxide. 20

The present invention also provides a process for bleaching hair which comprises applying to the hair a composition as defined above and 0.5 to 3 parts per part of the composition by 25 weight of an oxidizing agent or solution which is hydrogen peroxide or a persalt or a mixture thereof, leaving them in contact with the hair for a sufficient time to bleach it, after which the hair is rinsed with water and the hair is dried. 25

The present invention further provides a process for dyeing hair which comprises applying to the hair a dyeing composition as defined above and 0.5 to 3 parts per part of the composition 30 by weight of an oxidizing agent or solution which is hydrogen peroxide or a persalt or a mixture thereof, leaving them in contact with the hair for a sufficient time to produce the desired colour and rinsing and drying the hair. 30

Preferred persalts are alkali metal persulphates, perborates and urea peroxide.

The composition may be mixed with the oxidizing agent or solution before application to the 35 hair. 35

The hair-dyeing or bleaching compositions are applied to hair in sufficient quantity to produce the desired shade or bleaching.

The invention is now further explained in the following Examples. The parts are expressed on a weight basis.

40

EXAMPLE 1

Oleic acid	10.4	40
45 98% triethanolamine	5.44	45
Mirapol A15	0.1	

1	Ceraphyl 60	0.1	
2	Cationic emulsion		
5	Q.2.7224	0.5	5
6	35% strength solution of		
10	sodium metabisulphite	1.3	10
7	Pentasodium salt of diethylene-		
15	triaminopentaacetic acid	2.4	15
8	Oxidation dyes:		
20	p-phenylenediamine	0.027	20
9	resorcinol	0.033	
10	meta-aminophenol	0.030	
15	Hydroquinone	0.15	25
16	20% aqueous ammonia	10	
20	Water q.s.	100	30

At the time of use, 100 g of this composition are diluted with 100 g of 20-volume (6% strength by weight) hydrogen peroxide and are then applied for 30 minutes to blond hair. After rinsing and washing, the hair is dyed to a pearly very light ash-blond shade.

EXAMPLE 2

The procedure is the same as in Example 1. 100 g of composition are diluted with 100 g of 6% weight strength (20-volume) hydrogen peroxide and applied to blond hair for 30 minutes.

40	Oleic acid	1.3	40
45	98% triethanolamine	0.68	45
45	Mirapol AZI	0.1	45

12	Ceraphyl 60	0.1	
	ABIL 9950	0.1	
5	35% strength solution of sodium metabisulphite	1.3	5
10	Pentasodium salt of diethylene- triaminopentaacetic acid	2.4	10
	Oxidation dyes:		
15	p-phenylenediamine	0.03	15
	m-aminophenol	0.03	
20	Hydroquinone	0.15	20
	20% aqueous ammonia	10	
25	Water q.s.	100	25
	30 Shade (on blond hair)	very light blond	30
	EXAMPLE 3		
	The procedure is the same as in Example 1. 100 g of composition are diluted with 100 g of 6% weight strength (20-volume) hydrogen peroxide and applied to blond hair for 30 minutes.		
35	Oleic acid	6.94	35
	98% triethanolamine	3.63	
40	Lexein CP 125	0.1	40
	Alkyldimethylhydroxyethyl-		
45	ammonium chloride	0.1	45
	Cationic emulsion		
50	Q.2 7224	0.5	50
	35% strength solution of		

	sodium metabisulphite	1.3	
	Pentasodium salt of diethylene-		
5	triaminopentaacetic acid	2.4	5
	Oxidation dyes:		
10	p-phenylenediamine	0.03	10
	resorcinol	0.03	
15	m-aminophenol	0.03	15
	Hydroquinone	0.15	
20	20% aqueous ammonia	10	20
20	Water q.s.	100	

25 The hair is dyed to a very light blond shade. 25

EXAMPLE 4

30	Lauric acid	9.12	30
	98% triethanolamine	6.8	
35	Mirapol A15	0.1	35
	Catigene CS 40	0.1	
	ABIL 9905	0.1	
40	35% strength solution of		40
	sodium metabisulphite	1.3	
45	Pentasodium salt of diethylene-		45
	triaminopentaacetic acid	2.4	
	Oxidation dyes:		
50	p-phenylenediamine	0.8	50
	ortho-aminophenol	0.3	
55	resorcinol	0.7	55
	m-aminophenol	0.04	
60	2,4-diaminophenoxyethanol	0.07	60

Hydroquinone	0.15	
20% aqueous ammonia	10	
5 Water q.s.	100	5

At the time of use, 100 g of this composition are diluted with 70 g of 30-volume hydrogen peroxide. The composition is applied to blond hair for 30 minutes. After rinsing and washing, 10 the hair is dyed to a chestnut brown shade.

EXAMPLES 5 TO 8

The procedure is the same as in Example 1. 100 g of composition are diluted with 100 g of 6% weight strength (20-volume) hydrogen peroxide and applied to blond hair for 30 minutes.

	EXAMPLES	5	6	7	8	
20	Lauric acid	9.12	9.12	9.12	9.12	
20	98% triethanolamine	6.8	6.8	6.8	6.8	20
25	Mirapol A15	0.1	0.1	-	-	
25	Lexein CP 125	-	-	0.1	-	25
30	Cartaretine F8	-	-	-	0.1	
30	Ammonyx 4002	0.1	-	-	-	30
	Alkyldimethylhydroxyethyl-					
35	ammonium chloride	-	0.1	-	-	35
	Noramium M2 CD (dimethyl-					
40	dilauryl ammonium chloride)	-	-	0.1	-	40
40	Arquad 2 HT 75	-	-	-	0.1	
	ABIL 9905	0.5	0.5	0.5	0.5	
45	35% strength solution of					45

	sodium metabisulphite	1.3	1.3	1.3	1.3	
5	Pentasodium salt of diethylenetriaminopenta-					5
	acetic acid	2.4	2.4	2.4	2.4	
10	Oxidation dyes:					10
	p-phenylenediamine	0.44	0.48	0.03	0.03	
15	p-aminophenol	0.6	0.06	-	-	15
	o-aminophenol	-	0.13	-	-	
20	resorcinol	0.55	0.25	0.03	0.03	20
	m-aminophenol	0.12	0.08	0.03	0.03	
25	1-methyl-2-hydroxy-4-β-hydroxyethylaminobenzene	0.04	-	-	-	25
	2,4-diaminophenoxyethanol	0.05	0.06	-	-	
30	Hydroquinone	0.15	0.15	0.15	0.15	30
	20% aqueous ammonia	10	10	10	10	
35	Water q.s.	100	100	100	100	35
40	Shade (on blond hair)	golden chestnut	light chestnut	light blond	very light blond	40
45	EXAMPLES 9 TO 12	The procedure is the same as in Example 1. 100 g of composition are diluted with 100 g of 6% weight strength (20-volume) hydrogen peroxide and applied to blond hair for 30 minutes.				
50	EXAMPLES	9	10	11	12	50
	Oleic acid	1.6	1.6	1.58	1.58	

	2-Amino-2-methyl-1-propanol	0.5	0.5	-	-	
	N-methylaminoethanol	-	-	0.42	0.42	
5	Mirapol AZI	0.1	-	-	-	5
	Gafquat 734	-	0.1	0.1	0.1	
10	Ceraphyl 60	-	-	0.1	-	10
	Alkyldimethylhydroxy-					
15	ethylammonium chloride	0.1	0.1	-	-	15
	Genamine KDMF	-	-	-	0.1	
	Ucar Silicone ALE 56	-	-	0.5	-	
20	Cationic emulsion DC 929	2	2	-	-	20
	ABIL 9905	-	-	-	2	
25	35% strength solution of Na					25
	-metabisulphite	1.3	1.3	1.3	1.3	
30	Pentasodium salt of					30
	diethylenetriaminopenta-					
35	acetic acid	2.4	2.4	2.4	2.4	35
	Oxidation dyes:					
40	p-phenylenediamine	0.1	0.1	0.1	0.1	40
	p-aminophenol	0.04	0.04	0.04	0.04	
	resorcinol	0.05	0.05	0.05	0.05	
45	m-aminophenol	0.05	0.05	0.05	0.05	45
	2,4-diaminophenoxyethanol	0.01	0.01	0.01	0.01	
50	Hydroquinone	0.15	0.15	0.15	0.15	50
	20% aqueous ammonia	10	10	10	10	
55	Distilled water q.s.	100	100	100	100	55
		light	ash	pearly	light	
60		ash	blond	light	ash	60
		blond		ash	blond	
				blond		

The procedure is the same as in Example 1.
 100 g of composition are diluted with 100 g of 6% by weight (20-volume) hydrogen peroxide
 and applied to blond hair for 30 minutes.

5	EXAMPLES	13	14	15	5
10	Lauric acid	10.1	10.1	11.04	
10	98% triethanolamine	8.51	8.51	-	10
15	2-Amino-2-methyl-1-propanol	-	-	4.94	
15	Merquat 100	2	-	-	15
20	Ionene G1	-	0.1	0.1	
20	Alkyldimethylhydroxyethyl-				20
20	ammonium chloride	3	3	0.1	
25	Ethanol	11	11	-	
25	Propylene glycol	2	2	-	25
30	ABIL 9905	2.1	2.1	0.5	
30	35% strength solution of				30
35	Na metabisulphite	1.3	-	1.3	
35	Pentasodium salt of				35
35	diethylenetriaminopenta-				
40	acetic acid	2.4	2.4	2.4	
40	Oxidation dyes:				40

18	p-phenylenediamine	0.56	-	1.7	
	p-aminophenol	0.3	-	-	
5	resorcinol	0.31	-	0.6	5
	m-aminophenol	0.13	-	0.15	
10	o-aminophenol	0.18	-	0.35	10
	2-methylresorcinol	0.06	-	-	
15	2,4-diaminophenoxyethanol	-	-	0.6	15
	1-methyl-2-hydroxy-4-N-β-hydroxyethylaminobenzene	0.03	-	-	
20	Hydroquinone	0.15	-	0.15	20
	20% aqueous ammonia	10	10.6	10	
25	Distilled water q.s.	100	100	100	25
	Shade	golden	lightening	black	
30		chestnut			30

EXAMPLE 16

35	Oleic acid	6.02	35
	2-Amino-2-methyl-1,3-propanediol	1.98	
	Lexein QX 3000	0.1	
40	Ceraphyl 60	0.1	40
	Cationic emulsion Q 27224	0.5	
45	35% strength sodium metabisulphite	1.3	45
	Pentasodium salt of diethylenetriamino-		
50	pentaacetic acid	2.4	50

55	<u>Oxidation dyes:</u>		55
	p-Phenylenediamine	0.44	
	p-Aminophenol	0.6	

Resorcin L	0.55	
m-Aminophenol	0.12	
5 1-Methyl-2-hydroxy-4-B-hydroxy- ethylaminobenzene	0.04	5
10 2,4-Diaminophenoxyethanol	0.05	10
Hydroquinone	0.15	
20% aqueous ammonia	10	15
15 Water q.s.	100	

100 g of this composition are diluted at the time of use with 100 g of hydrogen peroxide of 20 6% weight strength. A quantity sufficient to impregnate the hair properly is applied to 90% white hair for 30 minutes and, after rinsing and washing, the hair is dyed to a golden light-chestnut shade. 20

EXAMPLE 17
25

Oleic acid	6.02	25
2-Amino-2-methyl-1,3-propanediol	1.98	
30 Mirapol AD1	0.1	30
Ceraphyl 60	0.1	
35 Cationic emulsion Q 27224	0.5	35
35% strength sodium metabisulphite	1.3	
40 Pentasodium salt of diethylenetriamino- pentaacetic acid	2.4	40
45		45
<u>Oxidation dyes:</u>		
p-Phenylenediamine	0.44	
50 p-Aminophenol	0.6	50

Resorcinol	0.55	
m-Aminophenol	0.12	
5 1-Methyl-2-hydroxy-4-β-hydroxy- ethylaminobenzene	0.04	5
10 2,4-Diaminophenoxyethanol	0.05	10
Hydroquinone	0.15	
15 20% aqueous ammonia	10	15
Water q.s.	100	

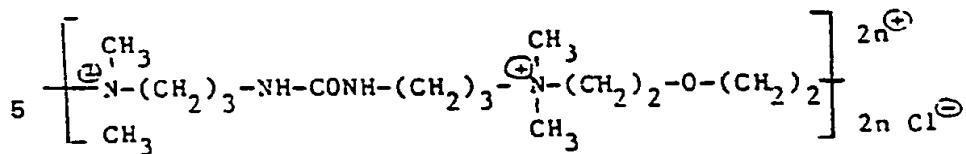
100 g of this composition are diluted at the time of use with 100 g of hydrogen peroxide at a
 20 concentration of 6% by weight. A sufficient quantity to impregnate the hair properly is applied
 to 90% white hair for 30 minutes and, after rinsing and washing, the hair is dyed to a golden
 light-chestnut shade. 20

EXAMPLE 18		
25 98% triethanolamine	6.80	25
30 Lauric acid	9.12	
30 Mirapol A15	0.1	30
35 Cetylpyridinium chloride	0.1	
35 ABIL B 9905	1	35
40 35% strength sodium metabisulphite	1.3	
40 Pentasodium salt of diethylenetri- aminopentaacetic acid	2.4	40
45		45
<u>Oxidation dyes:</u>		
50 p-Phenylenediamine	0.44	
50 p-Aminophenol	0.6	50

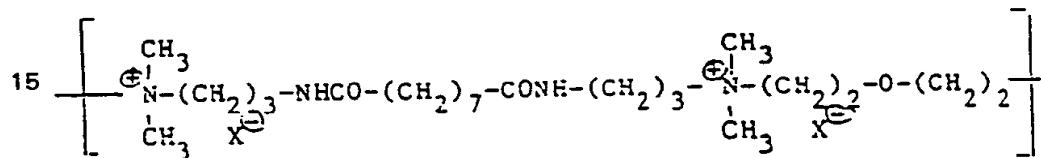
Resorcinol	0.55	
m-Aminophenol	0.12	
5 1-Methyl-2-hydroxy-4-β-hydroxy- ethylaminobenzene	0.04	5
10 2,4-Diaminophenoxyethanol	0.05	10
Hydroquinone	0.15	
15 20% aqueous ammonia	10	15
Water q.s.	100	20
20 100 g of this composition are diluted at the time of use with 100 g of hydrogen peroxide at a concentration of 6% by weight. A sufficient quantity to impregnate the hair properly is applied to 90% white hair for 30 minutes and, after rinsing and washing, the hair is of a golden chestnut shade.		25
25 Correspondence between trademarks and chemical composition:		
ABIL 9905		
30 $\text{CH}_3 - \text{Si} - \text{O} \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{Si} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array} \right]_p \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{Si} \\ \\ (\text{CH}_2)_3 \end{array} \right]_q \text{CH}_3$		30
35 $\begin{array}{c} \text{CH}_2 \\ \\ \text{CHOH} \end{array}$		35
40 $\begin{array}{c} \text{CH}_2 \\ \\ \text{H}_3\text{C} - \text{N}^{\oplus} - \text{CH}_3 \\ \\ \text{CH} \end{array}$		40
45 $\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3\text{COO}^{\ominus}$		45
ABIL 9950 Amphoteric silicone polymer of formula:		

50 $\text{CH}_3 - \text{Si} - \text{O} \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{Si} - \text{O} \\ \\ \text{CH}_3 \end{array} \right]_p \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{Si} - \text{O} \\ \\ (\text{CH}_2)_3 \end{array} \right]_q \text{CH}_3$		50
55 $\begin{array}{c} \text{CH}_2 \\ \\ \text{CHOH} \end{array}$		55
60 $\begin{array}{c} \text{CH}_2 \\ \\ \text{H}_3\text{C} - \text{CH}_2 - \text{CH}_2 - \text{COO}^{\ominus} \end{array}$		60
65		65

AMMONYX 4002	Dimethylstearylbenzylammonium chloride	
ARQUAT 2 HT 75	Dimethyldialkyl(hydrogenated tallow)-ammonium chloride	
CATIGENE CS 40	(Stepan company) Dimethylstearylbenzylammonium chloride	5
5		
CARTARETINE F8 (Sandoz)	Adipic acid/dimethylaminohydroxypropyl/diethylenetriamine polymer	
10		
CERAPHYL 60 (Van Dik)	Dimethyl-gamma-gluconamidopropyl-hydroxyethylammonium chloride (cationic surface agent).	
10		10
CATIONIC EMULSION DC 929 (Dow Corning company)		
Combination of:		
(i) amodimethicone,		
(ii) tallowtrimonium chloride of formula:		
15		15
$R_{11} - \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{N}^+ - \text{CH}_3 \\ \\ \text{CH}_3 \end{array} \right] \text{Cl}^-$		
20		20
where R_{11} denotes a mixture of C_{14-22} alkenyl and/or alkyl radicals derived from tallow fatty acids;		
(iii) NONOXYL 10 of formula:		
25		25
$C_9\text{H}_{19}-\text{C}_6\text{H}_4-(\text{OC}_2\text{H}_4)_{10}-\text{OH}$		
CATIONIC EMULSION Q2 7224 (Dow Corning company)		
Combination of		
30		30
(a) trimethylsilylamodimethicone		
(b) octoxynol 40 of formula:		
$C_8\text{H}_{17}-\text{C}_6\text{H}_4-(\text{OCH}_2\text{CH}_2)_n-\text{OH}$ where $n=40$		
35		35
(c) isolaureth-6 of formula:		
$C_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_n-\text{OH}$ where $n=6$		
35		35
(d) glycol		
40		40
GAFQUAT 734 (GAF Corporation)		
Quaternized copolymer of vinylpyrrolidone and of another copolymerizable monomer (M.W. approximately one million)		
GENAMINE KDMF (Hoechst): trimethylalkyl(C_{20-220})ammonium chloride		
IONENE G1 Quaternary polymer of formula		
45		45
$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{N}^+ - (\text{CH}_2)_3 - \text{CH}_3 \\ \\ \text{CH}_3 \end{array} \right] \text{Cl}^-$		
50		50
LEXEIN CP 125 (Inolex company)		
Hydrolysed animal protein substituted by an oleamidopropyldimethylamine radical.		
55		55
MERQUAT 100 (Merck)		
Dimethyldialkylammonium chloride homopolymer (M.W. approximately 100,000)		
LEXEIN QX 3000 (Inolex) Quaternized animal protein derived from collagen hydrolysates.		
MIRAPOL A 15 (Miranol company)		
Cationic polymer of formula:		



where n is approximately 6
10 MIRAPOL AZ1 (Miranol company)
Quaternary polyammonium polymer of formula:



20 NORAMIUM M2 CD
Dimethyldilauryl ammonium chloride
UCAR SILICONE ALE 56 (Union Carbide)
Cationic silicone polymer with a flash point of 60°C according to the ASTM standard D-93,
and, at a concentration of 35% of active substance, a viscosity of 11 centipoises at 25°C and a
25 basicity index of 0.24 milliequivalent/gram.

CLAIMS

1. A cosmetic composition suitable for dyeing or bleaching hair when mixed with an oxidizing solution, comprising, in an aqueous medium:

30 (a) at least one fatty acid soap,
(b) at least one cationic or amphoteric silicone polymer,
(c) at least one cationic surface-active agent,
(d) at least one alkaliifying agent, and
(e) at least one cationic polymer which is a quaternary polyammonium polymer, a vinylpyrroli-
35 done/dialkylaminoalkyl acrylate or methacrylate copolymer (quaternized or not quaternized), a poly(methacrylamidopropyltrimethylammonium chloride), a cationic protein, a polyaminoamide, a crosslinked polyaminoamide, an alkylated polyaminoamide or a mixture thereof.

2. A cosmetic composition suitable for dyeing hair when mixed with an oxidizing agent, comprising, in an aqueous medium:

40 (a) at least one fatty acid soap,
(b) at least one cationic or amphoteric silicone polymer,
(c) at least one cationic surface-active agent,
(d) at least one alkaliifying agent, and
(e) at least one cationic polymer which is a quaternary polyammonium polymer, a vinylpyrroli-
45 done/dialkylaminoalkyl acrylate or methacrylate copolymer (quaternized or not quaternized), a poly(methacrylamidopropyltrimethylammonium chloride), a cationic protein, a polyaminoamide, a crosslinked polyaminoamide, an alkylated polyaminoamide, a cationic cyclopolymer or a mixture thereof,

f) at least one oxidation dye precursor, and

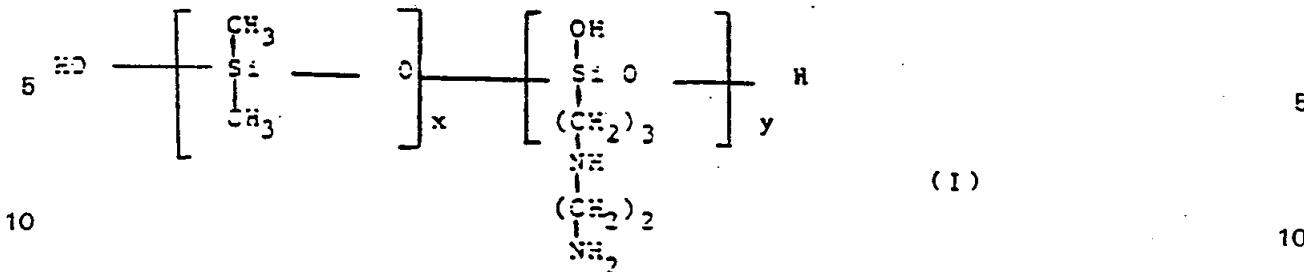
50 g) at least one reducing agent.
3. A composition according to claim 1 or 2 wherein the fatty acid soap is an alkali metal salt or alkanolamine salt of a C₁₂-C₁₈ fatty acid containing a saturated or unsaturated fatty chain, or a mixture thereof.

4. A composition according to any one of claims 1 to 3 wherein the fatty acid soap is present in an amount of from 1 to 25% by weight relative to the total weight of the composition.

5. A composition according to claim 4 wherein the fatty acid soap is present in an amount of from 2 to 20% by weight.

6. A composition according to any one of claims 1 to 5 wherein the cationic or amphoteric silicone polymer is a polysiloxane in which one or more of the silicon atoms in the chain carries an aliphatic amino group whose amine group is primary, secondary, tertiary or quaternary or is betainized, or a mixture thereof.

7. A composition according to claim 6 wherein the cationic silicone polymer is (i) a polymer known as "amodimethicone" of formula:



in which x and y, which may be identical or different, are integers such that the average
 15 molecular weight of the polymer is from 5,000 to 10,000;

(ii) a polymer of formula:



20 in which:

G is hydrogen or a phenyl, OH, or C_1-C_6 alkyl group;

20

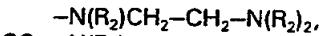
a is an integer from 0 to 3;

b is 0 or 1;

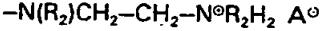
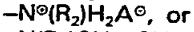
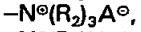
n is a number from 0 to 1,999 and m is a number from 1 to 2,000 such that the sum $n+m$
 25 is a number from 1 to 2,000;

25

R_1 is a monovalent group of formula $\text{C}_q\text{H}_{2q}\text{L}$ in which q is an integer from 2 to 8 and L is a
 group of formula:



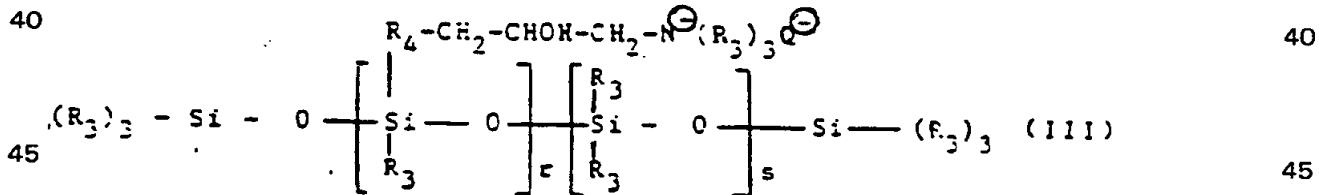
30



35 in which R_2 is hydrogen or a phenyl, benzyl, or saturated hydrocarbon group and A^\ominus is a halide
 ion;

35

(iii) a polymer of formula:



in which:

50 R_3 is a monovalent hydrocarbon group containing from 1 to 18 carbon atoms;

50

R_4 is a hydrocarbon group optionally containing a chain oxygen atom;

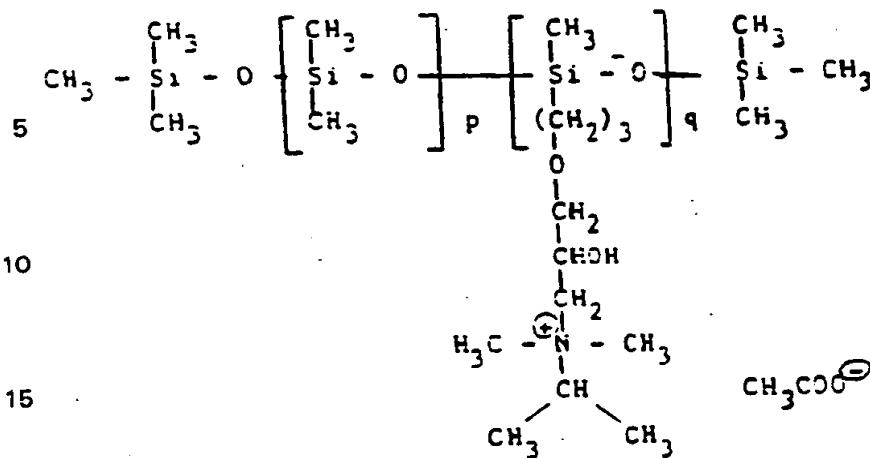
Q^\ominus is a halide ion;

r has a statistical average value of from 2 to 20; and

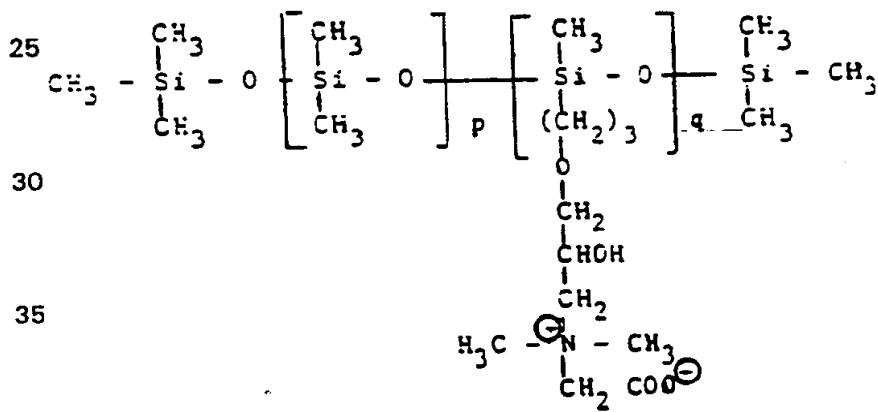
s has a statistical average value of from 20 to 200;

55 (iv) a polymer of formula:

55



20 wherein p and q are such that the average molecular weight is from 1,000 to 8,000, sold under 20
the trade name "ABIL 9905" by Goldschmidt; or
(v) an amphoteric silicone polymer of formula:



40 wherein p and q are such that the average molecular weight is from 1,000 to 8,000, sold under 40
the trade name ABIL 9950 by Goldschmidt.

8. A composition according to claim 7 wherein the cationic silicone polymer is as defined in 45
section (ii) wherein:

45 G is a methyl group;

a is O;

b is 1;

n is a number from 49 to 149 and m is a number from 1 to 10 such that the sum n+m is a 45
number from 50 to 150; and

50 R₂ is an alkyl group containing from 1 to 20 carbon atoms.

9. A composition according to claim 7 wherein the cationic silicone polymer is as defined in 50
section (iii) wherein:

R₃ is an alkyl or alkenyl group;

R₄ is a C₁-C₁₈ alkylene group or a C₁-C₁₈ alkyleneoxy group;

55 Q⁻ is a chloride ion;

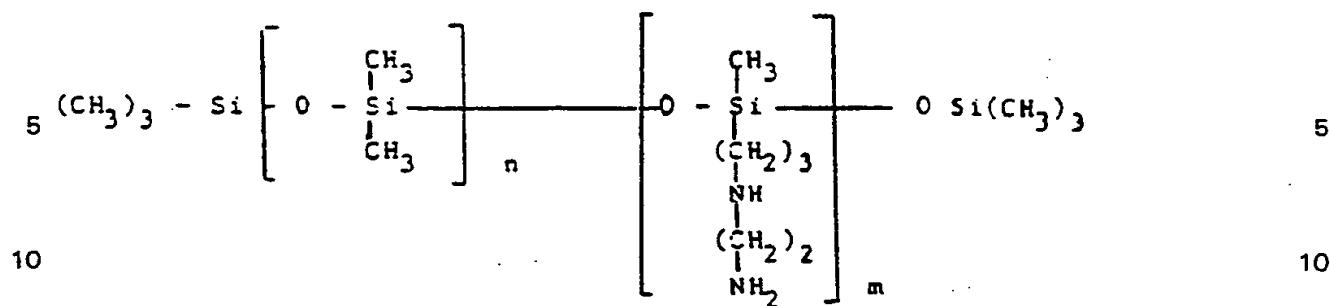
r has a statistical average value of from 2 to 8; and

s has a statistical average value of from 20 to 50.

10. A composition according to claim 9 wherein R₃ is a methyl group and R₄ is a C₁-C₈ 55
alkyleneoxy group.

60 11. A composition according to claim 7 wherein the cationic silicone polymer is:

(i) the polymer known as "trimethylsilylmodimethicone" of formula:



wherein n has a value of from 0 to 1,999 and m has a value of from 1 to 2,000 such that
15 m+n has a value of from 1 to 2,000, or

(ii) a polymer sold by Union Carbide under

(iii) a polymer sold by Union Carbide under the name Ocar Silicon ALE 50.

12. A composition according to any one of claims 1 to 11 wherein the cationic or amphoteric silicone polymer is present in an amount of from 0.05 to 5% by weight relative to the total weight of the composition.

20 13. A composition according to claim 12 wherein the cationic or amphoteric silicone polymer is present in an amount of from 0.1 to 3% by weight.

14. A composition according to any one of claims 1 to 13 wherein the cationic surface-active agent is a compound of formula:



in which

(1) B₁ and B₂ are both methyl groups.

ii) R₁ and R₂ are both methyl groups, R₃ and R₄ which may be identical or different, are each a linear aliphatic group.

ii) R_1 and R_2 , which may be identical or different, are each a linear aliphatic group.

35 iii) R_7 is a linear aliphatic group and R_8 is a methyl or benzyl group, or
 iii) R_7 is an alkylamidopropyl group and R_8 is an alkylacetate group, or
 iv) R_7 is a gamma-gluconamidopropyl group, an aliphatic group derived from a tallow fatty acid or a C_{16} - C_{18} alkyl group, and R_8 is a hydroxyethyl group, and
 X^0 is an anion; or

(2) R_5 is an alkylamidoethyl or alkenylamidoethyl group, wherein the alkyl or alkenyl moiety contains from 14 to 22 carbon atoms and originates from a tallow fatty acid, R_6 and R_7 form, together with the nitrogen to which they are attached, a 2-alkyl-4,5-dihydroimidazole heterocyclic ring wherein the alkyl moiety is derived from a tallow fatty acid, R_8 is a methyl group and X^\ominus is a methosulphate ion; or

(3) R_5 , R_6 and R_7 form, together with the nitrogen to which they are attached, a six membered aromatic heterocyclic ring, R_8 is a C_{14} – C_{18} alkyl group and X^{\ominus} is a halide anion; or a mixture thereof.

15. A composition according to claim 14 in which:

(1) R_5 and R_6 are both methyl groups.

50 *i*) R_5 and R_6 are both methyl groups,
ii) R_7 and R_8 , which may be identical or different, are each an alkyl group containing from 12 to 22 carbon atoms or an aliphatic group derived from at least one tallow fatty acid containing from 14 to 22 carbon atoms.

ii) R_7 is a linear alkyl group containing from 14 to 22 carbon atoms and R_8 is a methyl or benzyl group, or

iii) R_7 is an alkylamidopropyl group wherein the alkyl moiety contains from 14 to 22 carbon atoms and R_8 is an alkylacetate group wherein the alkyl moiety contains from 12 to 16 carbon atoms and

Y is a halide or methosulphato anion, or a mixture thereof.

16. A composition according to any one of claims 1 to 13 wherein the cationic surface-active agent is dimethyl dialkylammonium chloride sold under the name "Noraprimium M2-CDP".

active agent is dimethyl dialkylammonium chloride sold under the name "Noramium M2 CD"; 60 dimethyl dialkyl (hydrogenated tallow) ammonium chloride sold under the name "Arquat 2H 75", dimethyldialkyl(C₁₈)ammonium chloride sold under the name "Genamine DSAC" by Hoechst, trimethylalkyl(C₂₀-C₂₂)-ammonium chloride sold under the trade name "Genamine KDM-F" by Hoechst, cetylpyridinium chloride, dimethyldialkyl-(C₁₂-C₁₄)ammonium chloride, dimethyl-gamma-glycaminidropyrroniumhydroxethylammonium chloride sold under the trade name "Cetaphil 60" by

glyconamidopropylhydroxyethylammonium chloride sold under the trade name "Ceraphyl 60" by
65 van Dyk, dimethyldicetylammonium chloride sold under the trade name "Noranium M2 SH",
66

dimethylhydroxyethylalkyl(tallow)ammonium chloride, dimethylhydroxyethylacetylammonium chloride, or dimethylstearylbenzylammonium chloride sold under the trade names "Ammonyx 4002" by Onyx or "Catigene CS 40" by Stepan, or a mixture thereof.

17. A composition according to any one of claims 1 to 16 wherein the cationic surface-

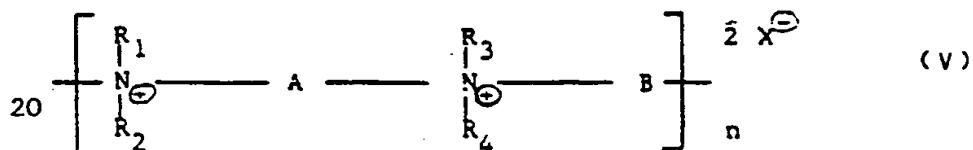
5 active agent is present in an amount of from 0.05 to 5% by weight relative to the total weight of the composition. 5

18. A composition according to any one of claims 1 to 17 wherein the alkalizing agent is sodium hydroxide, potassium hydroxide, aqueous ammonia or an alkanolamine.

19. A composition according to claim 18 wherein the alkalizing agent is mono-, di- or 10 triethanolamine, 2-amino-2-methyl-1-propanol, 2-amino-2-methyl-1,3-propanediol or triisopropanolamine.

20. A composition according to any one of claims 1 to 19 wherein the cationic polymer comprises a quaternary polyammonium polymer which is:

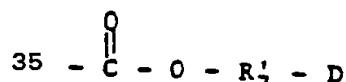
15 1) a polymer consisting of recurrent repeat units, which may be identical or different, of formula (V): 15



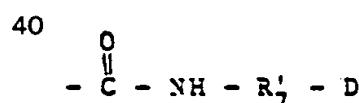
wherein

25 R₁, R₂, R₃ and R₄, which may be identical or different, each are an aliphatic, alicyclic or 25 arylaliphatic group containing from 1 to 20 carbon atoms or a C₁-C₆ hydroxylaliphatic group, or at least one of a pair of R₁ and R₂ and/or R₃ and R₄, form, together with the nitrogen to which they are attached, a heterocyclic ring optionally containing a second heteroatom other than nitrogen,

30 or R₁, R₂, R₃ and R₄, which may be identical or different, are each branched C₂-C₆ alkyl group 30 substituted by a nitrile, ester, acyl or amide group or by a group of formula



or



45 wherein

R' is an alkylene group, and

D is a quaternary ammonium group;

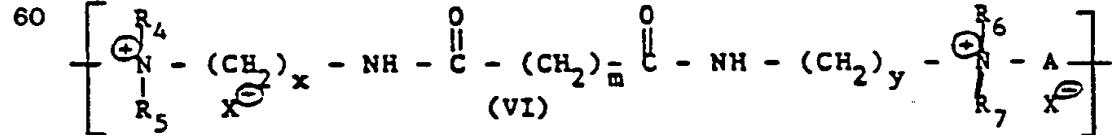
A and B, which may be identical or different, are each an aliphatic hydrocarbon group containing from 2 to 20 carbon atoms, which is linear or branched, saturated or unsaturated and 50 which optionally contains, in the main chain, one or more aromatic rings or one or more oxygen or sulphur atoms or one or more sulphonide, sulphone, disulphide, amine, alkylamine, quaternary ammonium, hydroxyl, ureido, amide or ester groups,

or A, R₁ and R₃, together with the two nitrogen atoms to which they are attached, form a piperazine ring;

55 each X⁹, which may be identical or different, is an anion derived from an inorganic or organic acid; and

n is such that the molecular weight of the polymer is from 1,000 to 100,000;

(2) a polymer consisting of repeat units, which may be identical or different, of formula (VI):



wherein:

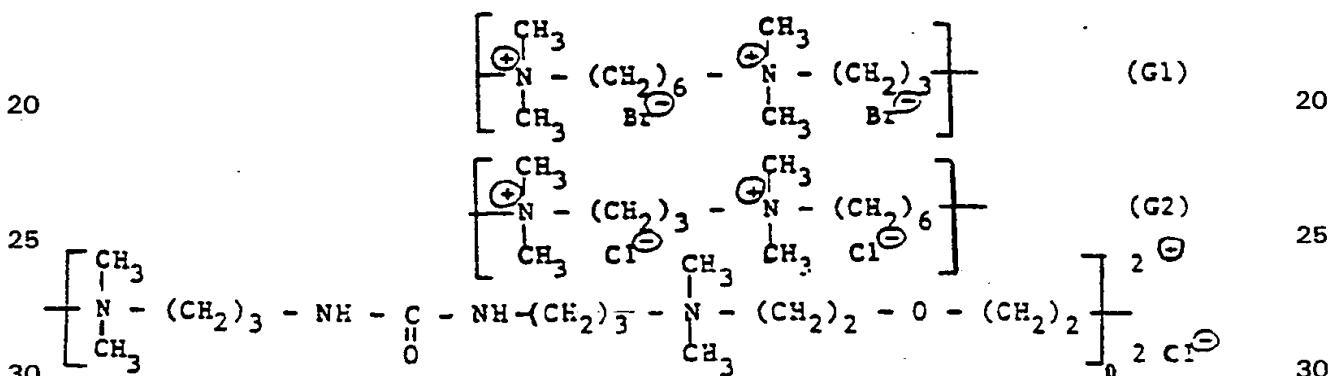
R_4 , R_5 , R_6 and R_7 , which may be identical or different, are each hydrogen, a methyl, ethyl, propyl, 2-hydroxyethyl or 2-hydroxypropyl group or a group of formula $-\text{CH}_2-\text{CH}_2-(\text{O}-\text{CH}_2-\text{CH}_2)-\text{OH}$ wherein ρ is an integer from 0 to 6;

5 with the proviso that R_4 , R_5 , R_6 and R_7 are not all simultaneously hydrogen;
 x and y, which may be identical or different, are each integers from 1 to 6;
 m is an integer 0 to 34;
 each X^{\ominus} , which may be identical or different, is a halogen anion, and
 A is a divalent hydrocarbon group optionally containing a chain oxygen atom.

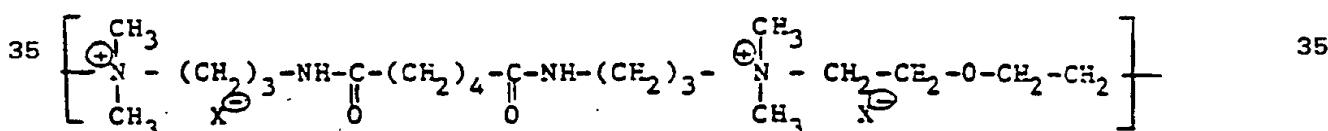
10 21. A composition according to claim 20 wherein A is a group of formula:

$$-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$$

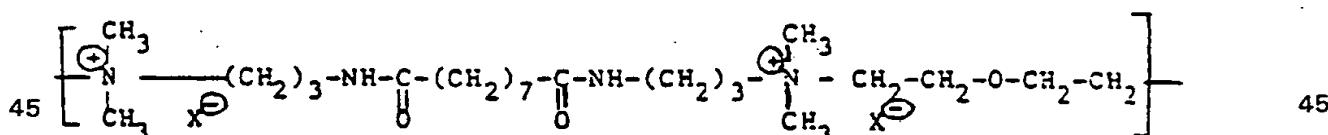
22. A composition according to claim 20 or 21 wherein the quaternary polyammonium 15 polymer consists of one of the repeat units:



wherein n is equal to approximately 6.



40, wherein each X, which may be identical or different, is a halogen.



wherein each X, which may be identical or different, is a halogen, or poly(dimethylbutenylammonium chloride) α,ω -bis(triethanolammonium chloride).

50 23. A composition according to any one of claims 1 to 22 wherein the cationic polymer is 50
present in an amount of from 0.05 to 3% relative to the total weight of the composition.

24. A composition according to any one of claims 1 to 23 wherein the cationic polymer comprises a cationic protein which is a chemically modified polypeptide bearing at least one amine or quaternary ammonium group at the end of, or grafted onto, the chain.

55 25. A composition according to claim 24 wherein the cationic protein is:

25. A composition according to claim 24 wherein the cationic protein is a collagen hydrolysate containing triethylammonium groups, such as the products sold under the trade name "Quat-Pro E" by Maybrook and called "Triethonium Hydrolyzed Collagen Ethosulfate" in the CTEA dictionary.

60 a collagen hydrosate containing trimethylammonium or trimethylstearylammmonium chloride groups, sold under the trade name "Quat-Pro S" by Maybrook and called "Steartrimonium

an animal protein hydrolysate containing trimethylbenzylammonium groups, such as the products sold under the trade name "Crotein BTA" by Croda and called "Benzyltrimonium hydro-

ducts sold under the trade name "Crotam-BTA" by Crotas and called "Benzylthiomethyl Hydrolyzed animal protein" in the CTFA dictionary;

comprising at least one alkyl group containing from 1 to 18 carbon atoms, such as Croquat L, whose polypeptide chain has an average molecular weight of approximately 2,500 and whose quaternary ammonium group contains a C_{12} alkyl group;

Croquat M, whose polypeptide chain has an average molecular weight of approximately 2,500 and whose quaternary ammonium group contains a C_{10} – C_{18} alkyl group;

Croquat S, whose polypeptide chain has an average molecular weight of approximately 2,700 and whose quaternary ammonium group contains a C_{18} alkyl group;

Crotein Q, whose polypeptide chain has an average molecular weight of the order of 12,000 and whose quaternary ammonium group contains at least one alkyl group containing from 1 to 10 18 carbon atoms; a protein of formula:



in which

20 A is a protein residue derived from a collagen protein hydrolysate,

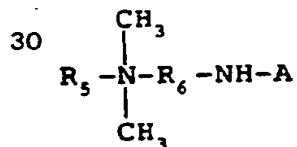
R₅ is a lipophilic group containing up to 30 carbon atoms.

R_6 is an alkylene group containing from 1 to 6 carbon atoms; and

X⁰ is an anion, the protein having a molecular weight of from 1,500 and 10,000; or an animal protein hydrolysate bearing dimethylamine groups, sold under the name of "Lexein

25 CP 125" by Inolex and referred to by the name "Oleamidopropyl dimethylamine hydrolyzed animal protein" in the CTFA dictionary.

26. A composition according to claim 25 wherein the cationic protein is a protein of formula:



35 wherein A, R₅ and R₆ are as defined in claim 25, having a molecular weight of from 2,000 to 5,000 and is a product sold under the trade name "Lexein QX 3000" by Inolex and called "Cocotrimonium-Collagen Hydrolysate" in the CTFA dictionary.

40 27. A composition according to any one of claims 1 to 26 wherein the cationic polymer
comprises a polyaminoamide which is:

(i) a water-soluble polyaminoamide of

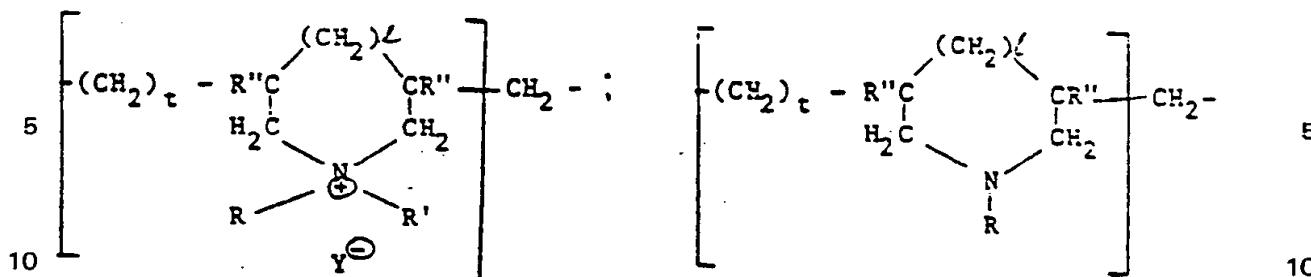
(ii) a polyaminopolyamide resulting from the condensation of a polyalkylenepolyamine with a polyaminoacid.

(iii) a polyaminoamide resulting from the condensation of a polyalkylenepolyamine with a polycarboxylic acid and alkylated with a difunctional agent, or

45 (iii) a polyaminoamide obtained by reaction of a polyalkylenepolyamine comprising two primary amine groups and at least one secondary amine group with a dicarboxylic acid, the molar ratio between the polyalkylenepolyamine and the dicarboxylic acid being from 0.8:1 to 1.4:1, the resultant polyaminoamide subsequently being reacted with epichlorohydrin, the molar ratio of epichlorohydrin to the secondary amine groups of the polyaminoamide being from 0.5:1 to

50 1.8:1.

28. A composition according to claim 2, or any one of claims 3 to 27 when appendant to claim 2, wherein the cationic polymer comprises a cationic cyclopolymer which is a polymer consisting of repeat units, which may be identical or different, of formula (VII) or a polymer consisting of repeat units, which may be identical or different, of formula (VIII)



in which:

I and t are each 0 or 1 such that the sum I+t is 1,

15 each R'', which may be identical or different, is hydrogen or a methyl group;
R and R', which may be identical or different, are each an alkyl group containing from 1 to 22
carbon atoms, a hydroxyalkyl group or a lower amidoalkyl group, or R and R' form, together
with the nitrogen to which they are attached, a heterocyclic group;

20 or a copolymer comprising units of formula (VII) or (VIII) and units derived from acrylamide or
diacetoneacrylamide;

and Y⁰ is an anion.

25 29. A composition according to claim 28 wherein at least one of R and R', which may be
identical or different, is a hydroxyalkyl group wherein the alkyl moiety contains from 1 to 5
carbon atoms or form, together with the nitrogen to which they are attached, a piperidyl or

25 morpholinyl group.

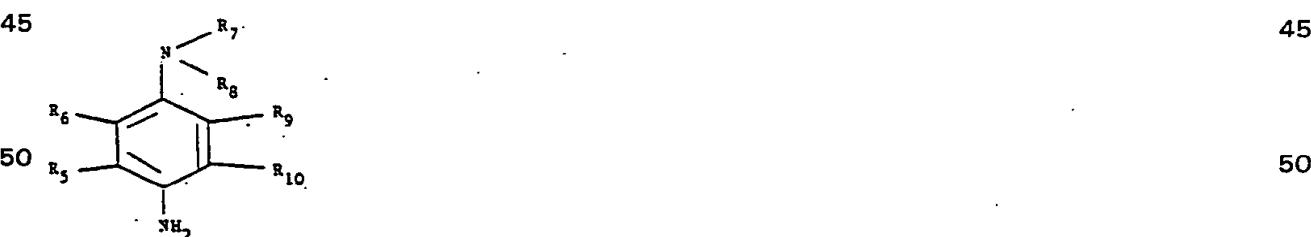
3. A composition according to claim 28 or 29 wherein the cationic cyclopolymer is a
homopolymer of dimethyldiallylammonium chloride having a molecular weight of less than
100,000 and sold by Merck under the trade name "Merquat 100" or a copolymer of dimethyldi-
allylammonium chloride and an acrylamide having a molecular weight of more than 500,000 and
30 sold under the trade name of "Merquat 550" by Merck.

31. A composition according to any one of claims 1 to 30 wherein the cationic polymer is
present in an amount of from 0.05 to 5% by weight relative to the total weight of the
composition.

32. A composition according to claim 2, or any one of claims 3 to 31 when appendant to
35 claim 2, wherein the reducing agent is thioglycolic acid, thiolactic acid, ammonium thiolactate or
sodium metabisulphite and is present in an amount of from 0.5 to 2% by weight relative to the
total weight of the composition.

33. A composition according to claim 2, or any one of claims 3 to 32 when appendant to
claim 2, wherein the oxidation dye precursor is an oxidation base which is a diamine, monoami-
40 nophenol or diaminophenol, a modifier which is a meta-diamine, meta-aminophenol, phenol or
polyphenol or a coupler.

34. A composition according to claim 33 wherein the oxidation base is a compound of
formula:



55 55 in which:

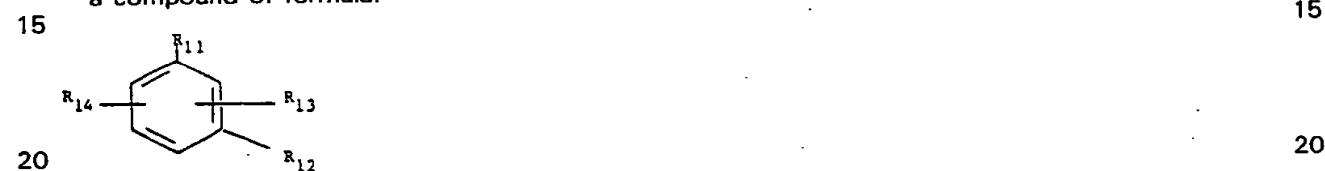
R₇ and R₈, which may be identical or different, are each hydrogen or a straight or branched
chain lower alkyl, mono- or polyhydroxylated alkyl, piperidinoalkyl, carbamylalkyl, dialkylcarbamyl-
alkyl, aminoalkyl, monoalkylaminoalkyl, dialkylaminoalkyl, omega-amino-sulphonylalkyl, carboxyl-
alkyl, alkylsulphonamidoalkyl, arylsulphonamidoalkyl, morpholinoalkyl, acylaminoalkyl, sulphoalkyl or
60 alkoxyalkyl group, in which groups the alkyl moiety contains from 1 to 4 carbon atoms;
or R₇ and R₈ form, together with the nitrogen to which they are attached, a morpholine or
piperidine heterocyclic group; and

R₅, R₆, R₉ and R₁₀, which may be identical or different, are each hydrogen, a halogen, a lower
alkyl group, or a group of formula -OZ wherein Z is a hydroxyalkyl, alkoxyalkyl, acylaminoalkyl,
65 carbalkoxyaminoalkyl, mesylaminoalkyl, ureidoalkyl, aminoalkyl, or mono- or dialkylaminoalkyl

group; or
their hydrochloride, hydrobromide, sulphate or tartrate salts;
p-aminophenol or a homologue thereof whose aromatic nucleus is substituted by at least one methyl group or by chlorine; or

5 5 N-methyl-p-aminophenol, a heterocyclic derivative of pyridine or of benzomorpholine, 5-aminoindole, orthoaminophenol, p-aminodiphenylamine or an ortho-phenylenediamine or a substituted derivative thereof;
the oxidation base being present in an amount of from 0.01 to 5% by weight relative to the total weight of the composition.

10 10 35. A composition according to claim 34 wherein at least one of R₅, R₆, R₉ and R₁₀, which may each be identical or different, is a lower alkyl group containing from 1 to 4 carbon atoms.
36. A composition according to any one of claims 33 to 35 which also comprises at least one coupler which is:
a compound of formula:



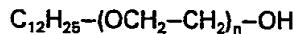
wherein:
R₁₁ and R₁₂, which may be identical or different, are each a hydroxyl group or a group of formula -NHR, wherein R is hydrogen or an acyl, ureido, carbalkoxy, carbamylalkyl, alkyl, dialkylcarbamylalkyl, hydroxyalkyl or mesylaminoalkyl group, one of R₁₁ and R₁₂ also being able to be hydrogen or an alkoxy or alkyl group, provided that the other is a hydroxyl group;
R₁₃ and R₁₄, which may be identical or different, are each hydrogen or a halogen, an amino, alkylamino, acylamino, ureido or branched or linear alkyl group or a group of formula OZ wherein Z is a hydroxyalkyl polyhydroxyalkyl, alkoxyalkyl, mesylaminoalkyl, acylaminoalkyl, ureidoalkyl or carbalkoxyalkyl group;
alpha-naphthol; or
a heterocyclic compound derived from benzomorpholine, pyridine, a pyrazolone or a diketone compound;
35 35 the coupler being present in an amount of from 0.001 to 5% by weight relative to the total weight of the composition.
37. A composition according to any one of claims 1 to 36 wherein the cationic silicone polymer used is in the form of an emulsion containing the silicone polymer and at least one nonionic or cationic surface agent which is:
40 40 the cationic emulsion "Dow Corning 929" sold by Dow Corning and which is a combination of
a) "amodimethicone" as defined in claim 7;
b) trimethylalkyl(tallow)ammonium chloride of formula:



50 50 wherein R₄ is a mixture of alkenyl and/or alkyl groups containing from 14 to 22 carbon atoms, derived from a tallow fatty acid; and
c) polyoxyethylenated nonylphenol of formula:
C₉H₁₉-C₆H₄-(OC₂H₄)₁₀-OH; or

55 55 the emulsion sold under the trade name "Dow Corning Q2 7224" by Dow Corning, and which is a combination of:
a) trimethylsilylamodimethicone as hereinbefore defined,
b) polyoxyethylenated octylphenol of formula:
C₈H₁₇-C₆H₄-(OCH₂CH₂)_n-OH

60 60 wherein n is 40;
c) polyoxyethylenated lauryl alcohol of formula:



wherein n is 6; and

d) glycol.

5 38. A composition according to any one of claims 1 to 37 which additionally comprises at least one adjuvant which is a solvent, fatty amide, fatty alcohol, nonionic or amphoteric surface agent, sequestering agent, antioxidant or perfume. 5

39. A composition according to claim 1 or 2 substantially as hereinbefore described with reference to any one of Examples 1 to 18.

10 40. A process for bleaching hair which comprises applying to the hair a composition as defined in any one of claims 1, or 3 to 29, 31 or 37 to 39 when appendant to claim 1, and 0.5 to 3 parts per part of the composition by weight of an oxidizing agent or solution which is hydrogen peroxide, or a persalt or a mixture thereof, leaving them in contact with the hair for a sufficient time to bleach it, after which the hair is rinsed with water and the hair is dried. 10

15 41. A process for dyeing hair which comprises applying to the hair a composition as defined in any one of claims 2, or 3 to 39 when appendant to claim 2, and 0.5 to 3 parts per part of the composition by weight of an oxidizing agent or solution which is hydrogen peroxide or a persalt or a mixture thereof, leaving them in contact with the hair for a sufficient time to produce the desired colour and rinsing and drying the hair. 15

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